AD-A120 863 ANALYTICAL METHODS DEVELOPMENT FOR DIMETHYL 1/
METHYLPHOSPHONATE DIISOPROPYL..(U) LITTLE (ARTHUR D)
INC CAMBRIDGE MA R FASANO ET AL. SEP 82
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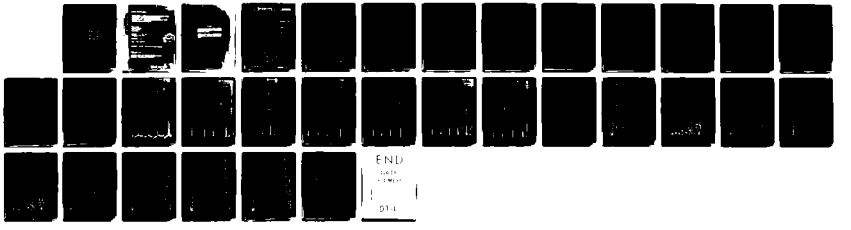
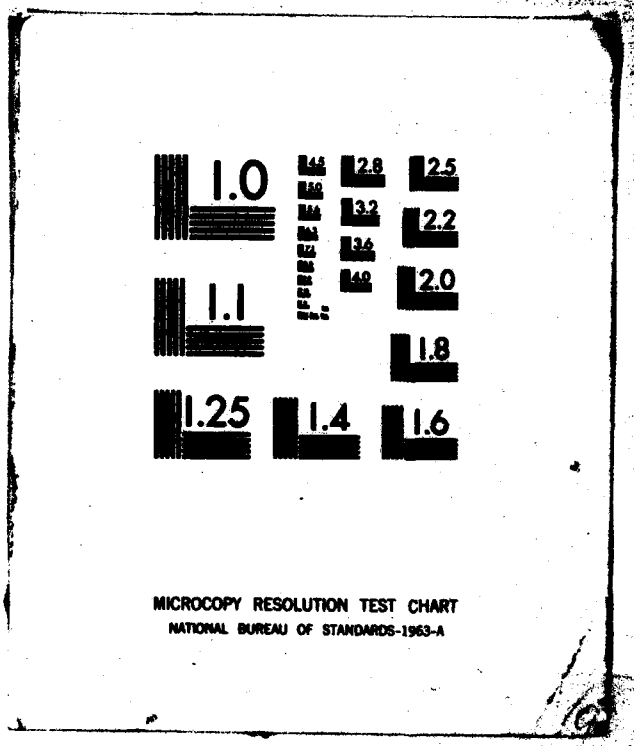
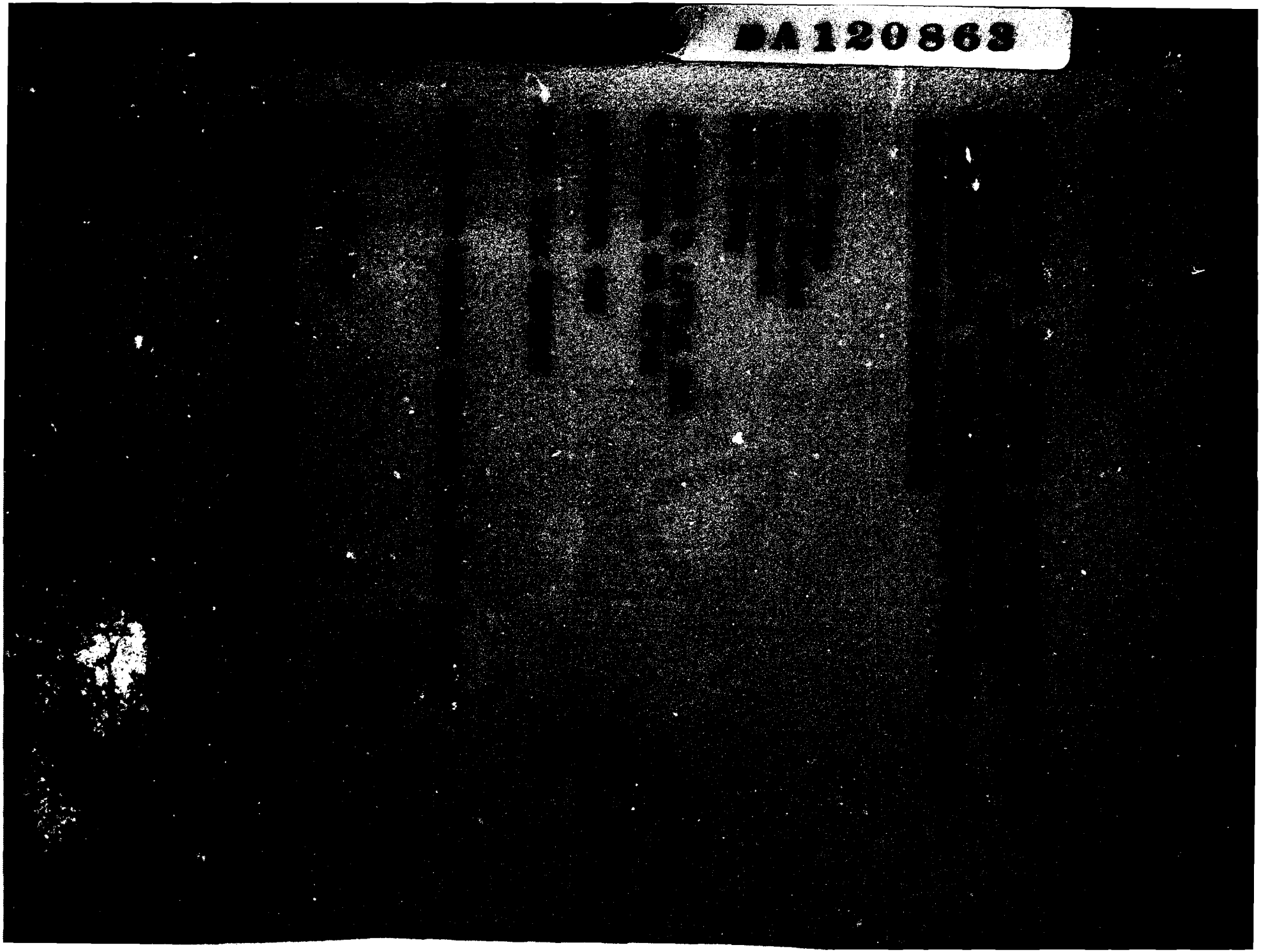



1.0
1.1
1.25
1.4
1.6
2.8
3.2
3.6
4.0
2.5
2.2
2.0
1.8
MICROCOPY RESOLUTION TEST CHART
NATIONAL BUREAU OF STANDARDS-1963-A



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Analytical Methods Development for Dimethyl methylphosphonate, Diisopropyl methylphosphonate and Trimethyl phosphate

Final Report

[redacted]

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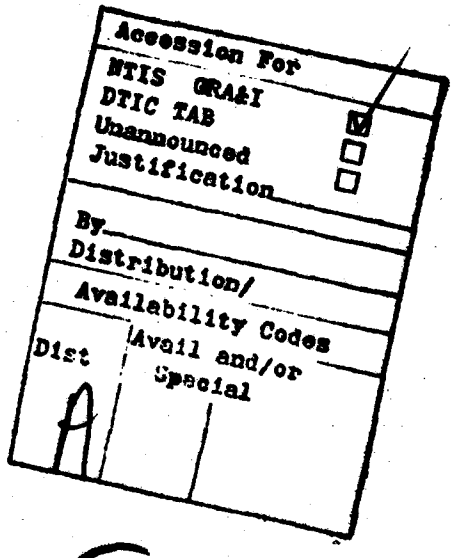
Diisopropyl methylphosphonate (DIMP)
Dimethyl methylphosphonate (DMMP)
Trimethyl phosphate (TMP)
Gas Chromatography/Flame Photometric Detector (GC/FPD)

[redacted]

A gas chromatographic [redacted] developed to [redacted] were performed [redacted] in presence of [redacted]

[redacted]

TABLE OF CONTENTS



LIST OF FIGURES

SUMMARY

A gas chromatographic system employing a Flame Photometric Detector (GC/FPD) was used to develop a method for the determination of Dimethyl methylphosphonate (DMMP), Diisopropyl methylphosphonate (DIMP) and Trimethyl phosphate (TMP) in aqueous samples under Task R902.35.14. The precision and accuracy of the developed method was determined from the analysis of aqueous samples spiked with 4.92 to 98.40 µg/L of DIMP in the presence of 10 mg/L each of DMMP and TMP. The detection limit at the 90% confidence level, calculated by the method of Hubaux and Vos, is 9.05 µg/L of DIMP in the presence of 10 mg/L each of DMMP and TMP.

INTRODUCTION

In May 1974, diisopropyl methylphosphonate (DIMP) and dicyclopentadiene (DCPD) were detected in surface water draining from a marshy bay on the northern boundary of Rocky Mountain Arsenal (RMA). In September 1974, a dike, north of the bog, was constructed to eliminate any off-post surface drainage.

As a result of observation of these two arsenal related compounds, a program of groundwater and surface water surveillance was initiated. Nineteen additional compounds were detected through gas chromatograph/mass spectrometer qualitative analysis in the groundwater near the northern boundary. Among these potential pollutants were the compounds dimethyl methylphosphonate (DMMP) and trimethylphosphate (TMP). Continued surveillance of RMA groundwater via gas chromatographic quantitative techniques has failed to demonstrate that these compounds represented a potential for migration off post.

During a contaminant leaching study contract effort in July 1980, Basin F liquid was to be analyzed to determine the concentration of DIMP. Instead of finding DIMP previously determined by the Government, the contractor instead identified the material as DMMP. The apparent error in reporting DIMP values, and the presence of significant concentrations of DMMP in a known source material (Basin F) indicated the possibility that DIMP values previously reported by the Government could be suspect.

In light of the error associated with the identification of the suspect contaminant species a chromatographic method was required which would resolve DIMP, DMMP and TMP. Additionally the method should be required to detect 10 ppb of DIMP in the presence of 10 ppm of DMMP and TMP.

I. ANALYTICAL METHOD

1. Application:

The method described in this report is for the quantification of Diisopropyl methylphosphonate (DIMP) in the presence of Dimethyl methylphosphonate (DMMP) and Trimethyl phosphate (TMP).

a. Tested Concentration Range: The tested concentration ranges are 4.9 to 98.4 µg/L DIMP in the presence of 10 mg/L of each DMMP and TMP.

b. Sensitivity: The following picograms of material injected on column give the listed peak height response in centimeters:

Compound	Pg injected	Peak Height (cm)
DIMP	25	0.79
DMMP	25	0.84
TMP	25	0.84

c. Detection Limit: The detection limit of DIMP calculated by the method of Hubaux and Vos, from standard water in the presence of 10 mg/L of DMMP and TMP, is 9.05 µg/L.

d. Interferences: No interferences were detected while developing the analytical method.

e. Analysis Rate: After sample preparation and instrument calibration, one analyst can analyze 20 samples in an eight-hour day.

2. Chemistry: The chemical structure of the three analytes are shown in Figure 1.

a. Diisopropyl methylphosphonate

C7H1703P

CAS RN1445-75-6

Boiling Point: 78-79°C (10 mm)

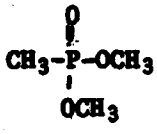
b. Dimethyl methylphosphonate

C3H903P

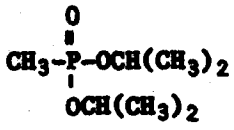
CAS RN121-45-9

Boiling Point: 181°C

Dimethyl methylphosphonate



Diisopropyl methylphosphonate



Trimethyl phosphate

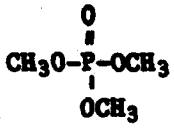
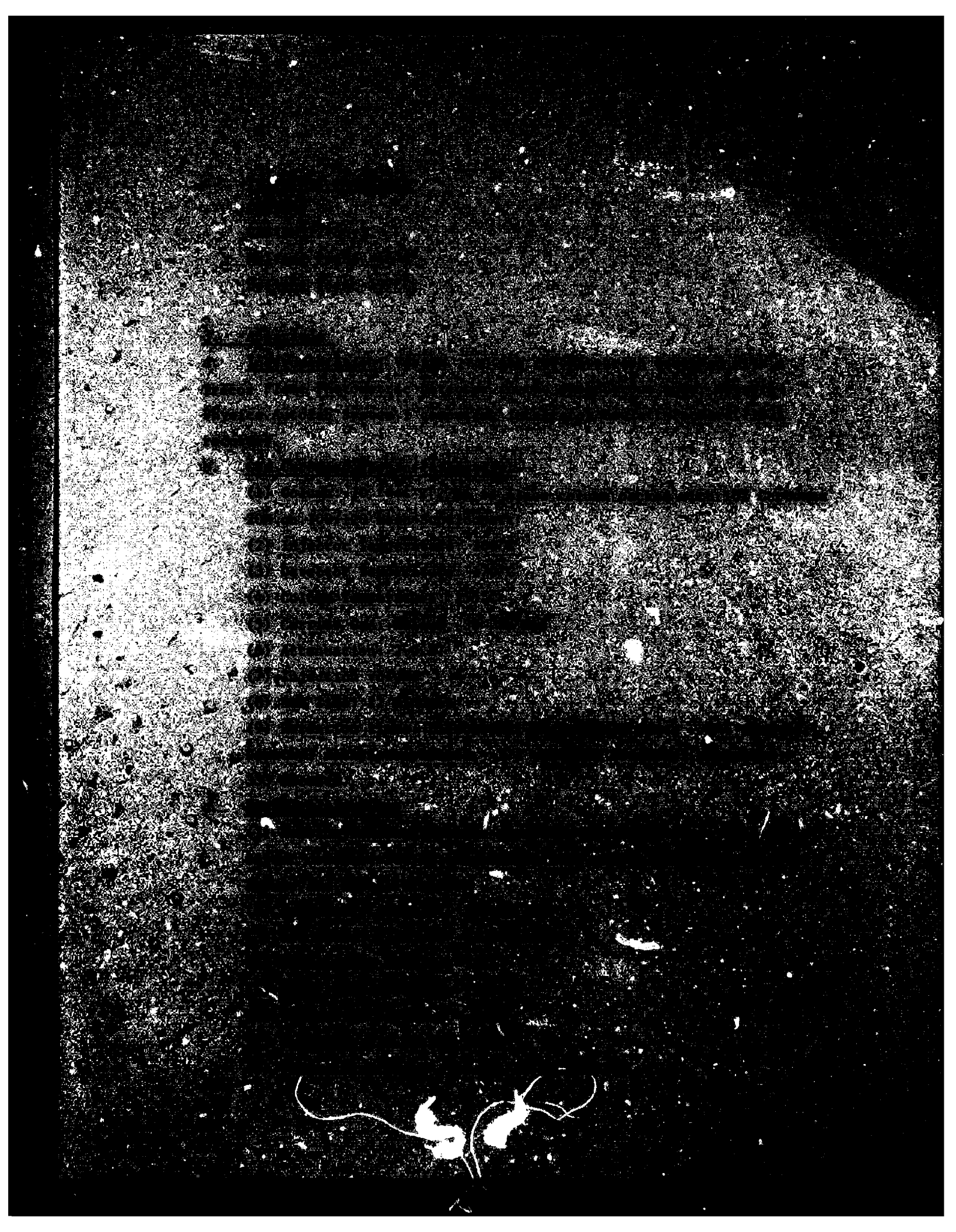


FIGURE 1

Chemical Structure of DIMP, DMMP and TMP



d. Chemicals:

(1) Methylene Chloride, HPLC grade

(2) Acetone, HPLC grade

(3) Sodium Sulfate, granular, anhydrous; extracted with methylene chloride, dried at 100°C, cooled and stored in clean glass screw capped Teflon® lined bottles.

(4) Sodium Chloride, anhydrous, reagent grade

(5) Diisopropyl methylphosphonate, Army-110-PA-249

(6) Dimethyl methylphosphonate; Army interim SARMS

(7) Trimethyl phosphate; Army - interim SARMS

4: Standards:

a. Calibration Standards:

(1) Stock A: Dilute 2.5 µL DIMP to 25 mL with HPLC grade acetone to give a 98.4 mg/L solution.

(2) Stock B: Dilute 220 µL DMMP and 210 µL TMP to 25 mL with HPLC grade acetone to give a 10.13 mg/mL DMMP and 10.04 mg/mL TMP solution.

(3) Prepare the following calibration standards by taking the listed volumes of Stock A and Stock B in a 10 mL volumetric flask and diluting to volume with methylene chloride:

			Concentration mg/L		
Cal. Std.	µL Stock A	µL Stock B	DIMP	DMMP	TMP
1	25	250	0.246	253.2	251.5
2	100	250	0.984	253.2	251.5
3	500	250	4.92	253.2	251.5
4	1,000	250	9.84	253.2	251.5

b. Control Spikes: Standard water was used as the aqueous media spiked. Prepare standard water as follows: 2.96g Na_2SO_4 and 3.3 g NaCl in 2 L Milli-Q water. One-hundred milliliter aliquots from the 2L solution of chloride and sulfate were transferred to 1L volumetrics and diluted with additional Milli-Q water yielding 100 mg/L solutions of the salts. The following volumes of stock solutions were spiked into 1 L standard water solutions (100 mg/L each salt).

Control Spike	mL Stock A	mL Stock B	Concentration DIMP µg/L	DMMP mg/L	TMP mg/L
1	0.05	1.0	4.92	10.13	10.04
2	0.10	1.0	9.84	10.13	10.04
3	0.20	1.0	19.68	10.13	10.04
4	0.50	1.0	49.20	10.13	10.04
5	1.00	1.0	98.40	10.13	10.04

Twenty control spikes and four control blanks were prepared (5 levels + 1 blank x 4 days) for subsequent extraction and analysis as stipulated in the USATHAMA QC protocol.

5. Sample Preparation

a. Extraction: Transfer the 1 L sample or control spike to a 2 L separatory funnel. Rinse the sample bottle with 100 mL CH_2Cl_2 and transfer the CH_2Cl_2 into the separatory funnel. Shake the separatory funnel vigorously, with venting, for one minute. Let the two phases separate and settle for three minutes. Transfer the CH_2Cl_2 extract to a 500 mL amber glass bottle. Repeat the extraction and transferal two times more.

b. Drying: Place clean glass wool over the Teflon® stopcock of a 125 mL separatory funnel and add ∿ 10 grams of clean dried Na_2SO_4. Rinse the glass wool and Na_2SO_4 with 10-15 mL of HPLC grade CH_2Cl_2. This solvent rinse is then discarded. Pass the sample extract through the sodium sulfate, glass wool layers and collect in a 500 mL Kuderna-Danish receiver equipped with clean boiling chip. Rinse the 125 mL separatory funnel with an additional 10-15 mL CH_2Cl_2 and add to the extract.

c. Concentration: Concentrate the extract by Kuderna Danish to less than 10 mL. Quantitatively transfer the concentrated extracts to a 10 mL volumetric flask and dilute to volume with CH_2Cl_2.

d. Analysis: A series of instrument calibration standards are prepared as outlined above, and analyzed during the same time period as the spiked samples. Calibration curves are established by plotting concentrations versus peak height. All calibration standards and samples should be analyzed in duplicate. Chromatograms of calibration

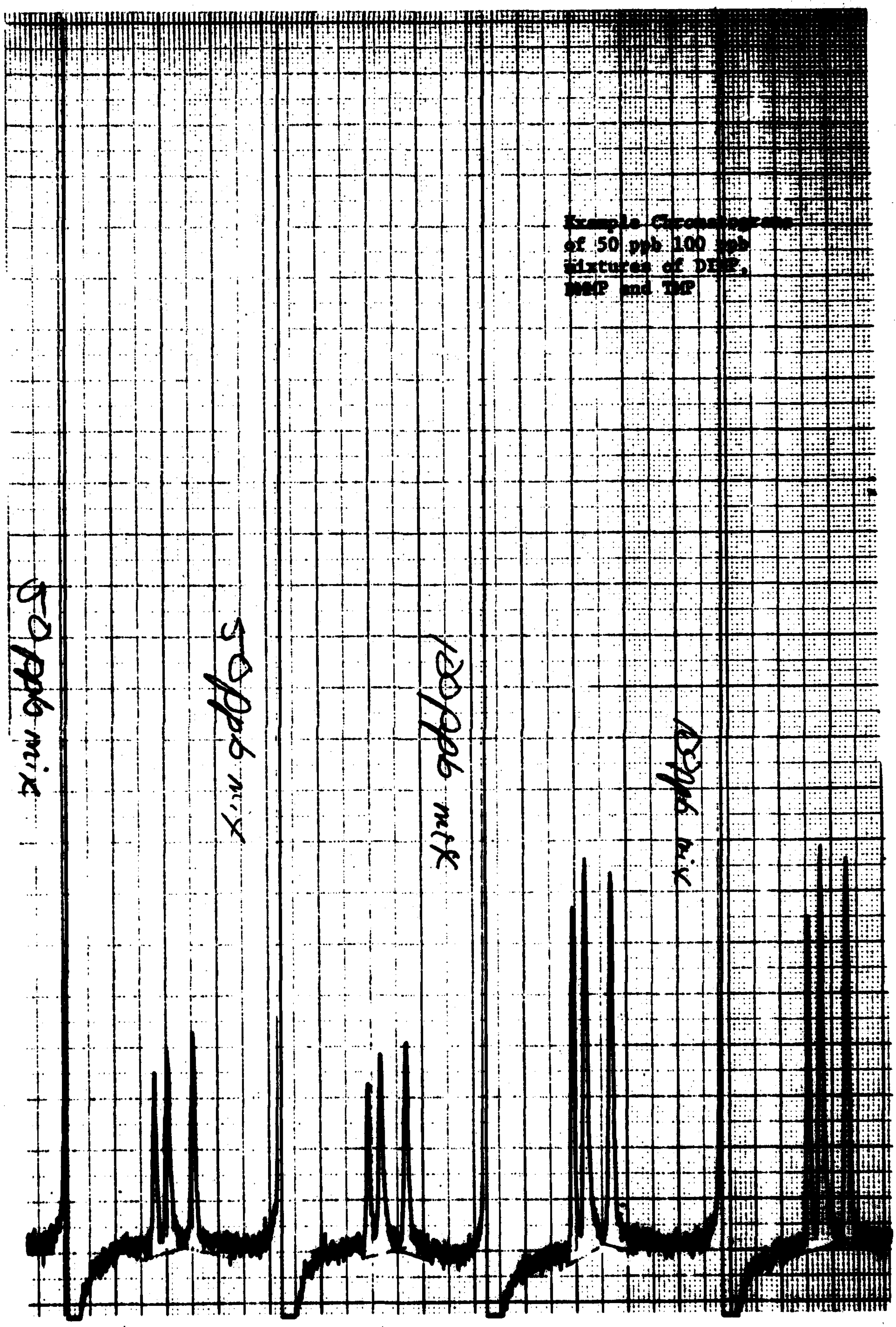
standards and spiked standard water samples used to generate precision and accuracy data are shown in Appendix A.

6. Calculations: Calculate µg/L for each analyte in each sample from daily calibration data. Using the control spike data, plot µg/L added versus µg/L found by the method of Hubaux and Vos using the detection limit (DL) tape supplied by USATHAMA. Correct field sample concentrations using the slope of this linear regression line. The results of the precision and accuracy tests for DIMP in the presence of 10 mg/mL DMMP and TMP may be found in Appendix B.

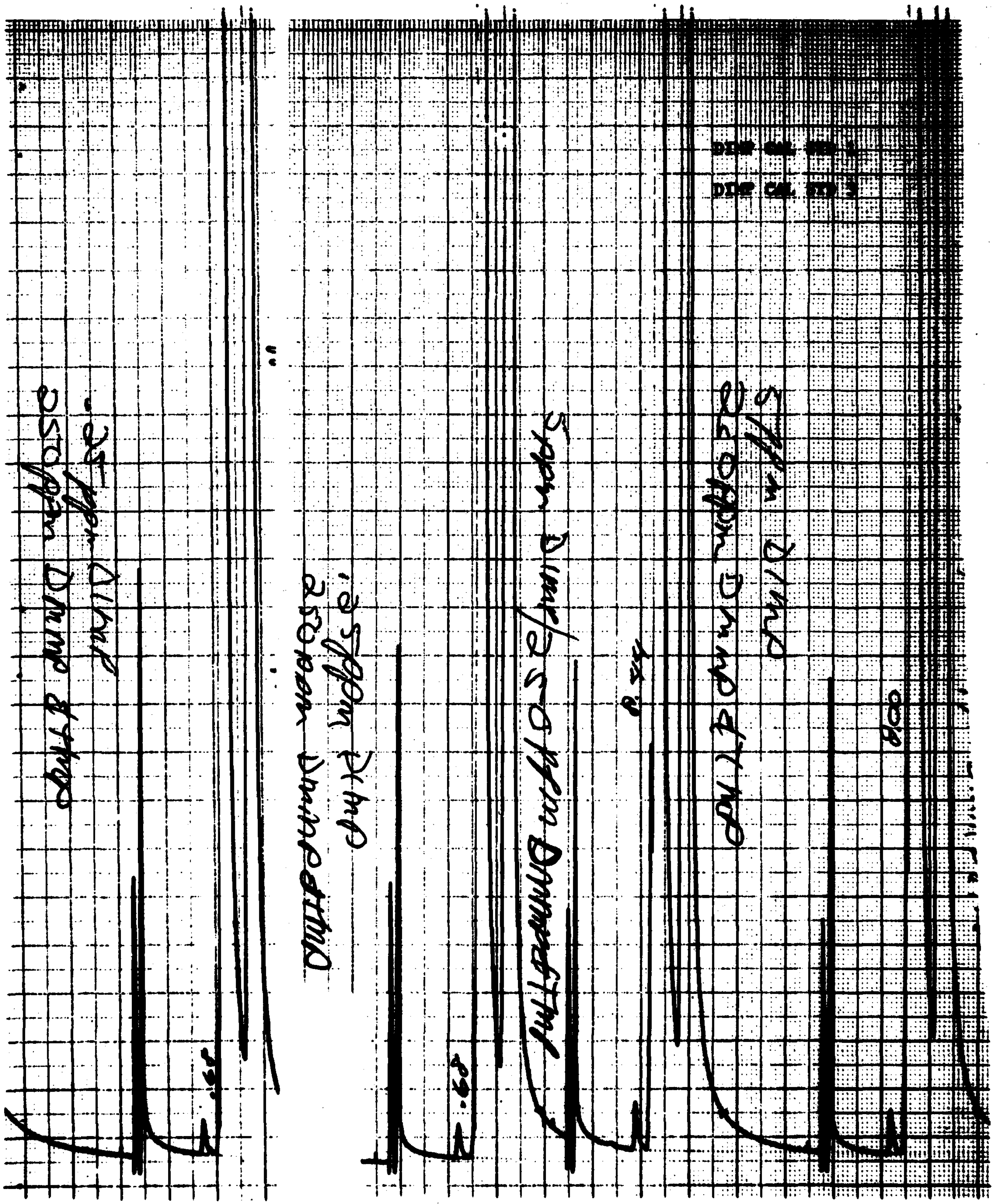
APPENDIX A

Chromatograms of Calibration Standards

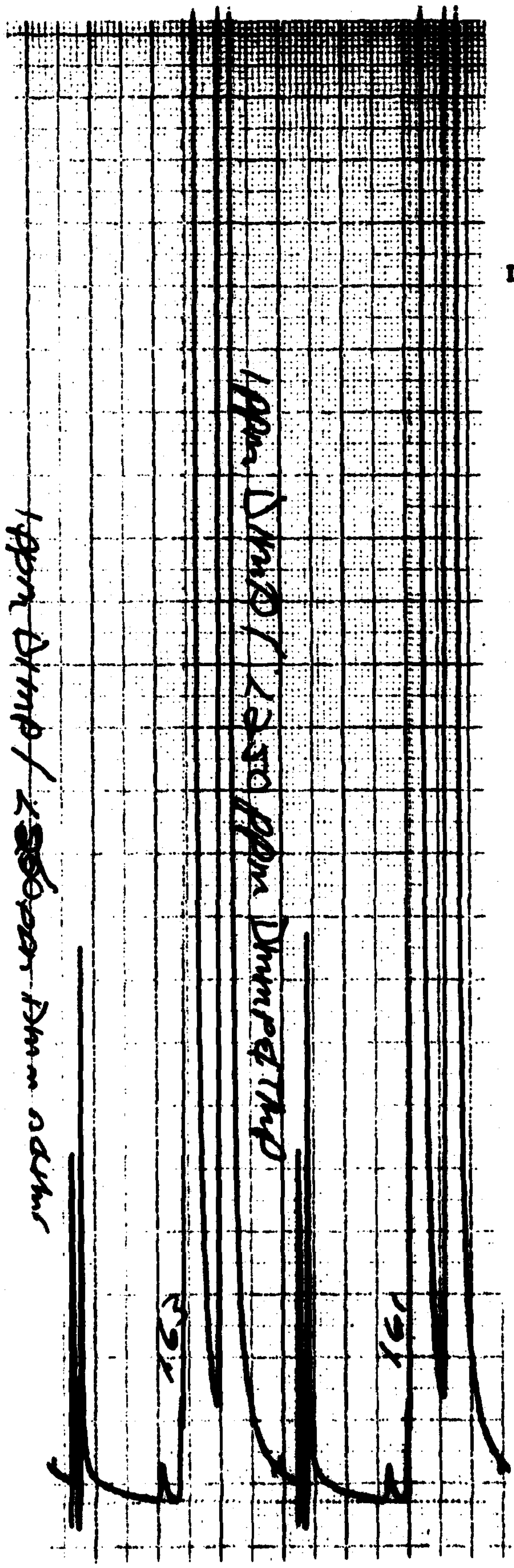
and Control Spike Samples of Diisopropyl methylphosphate

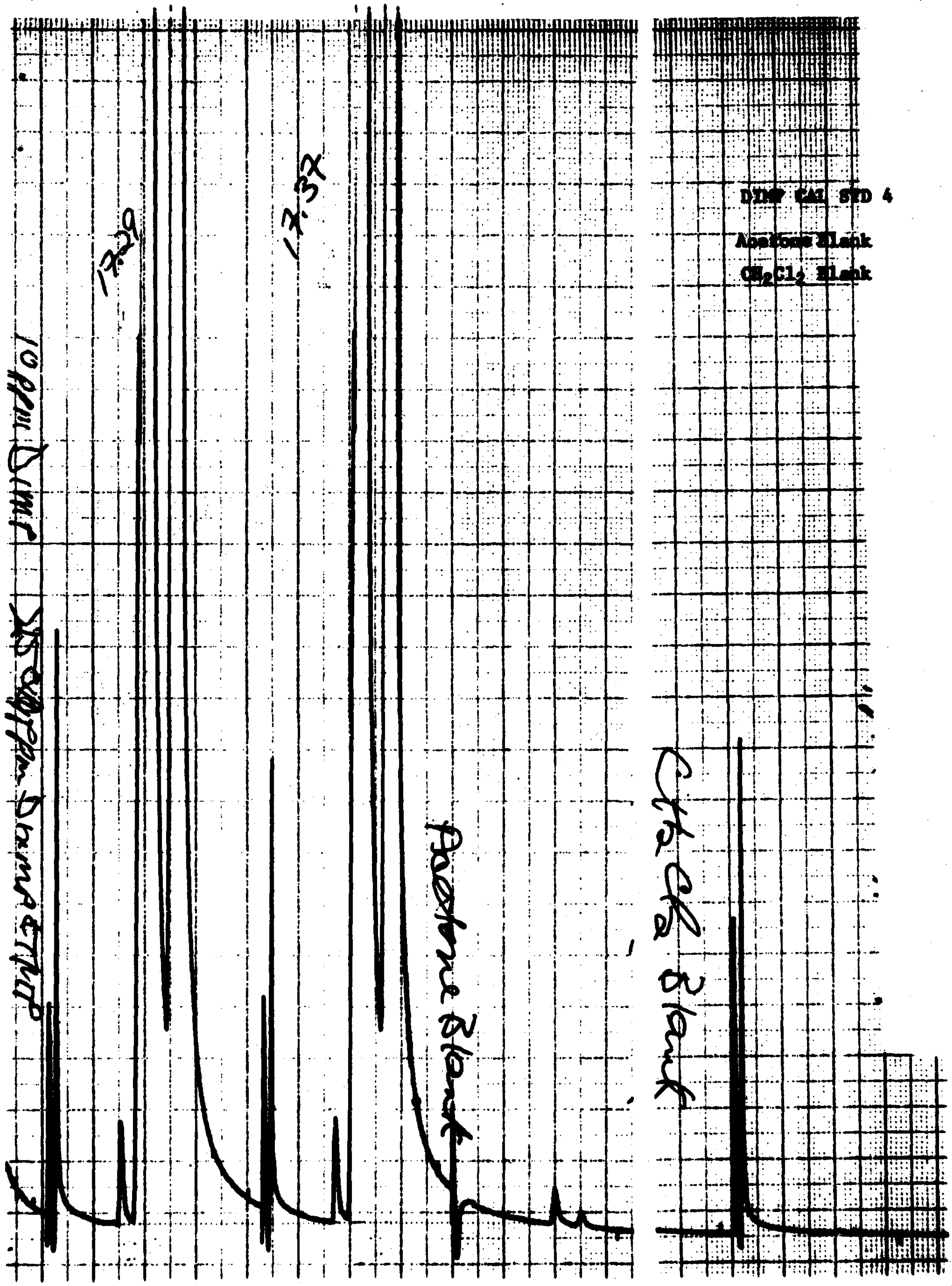


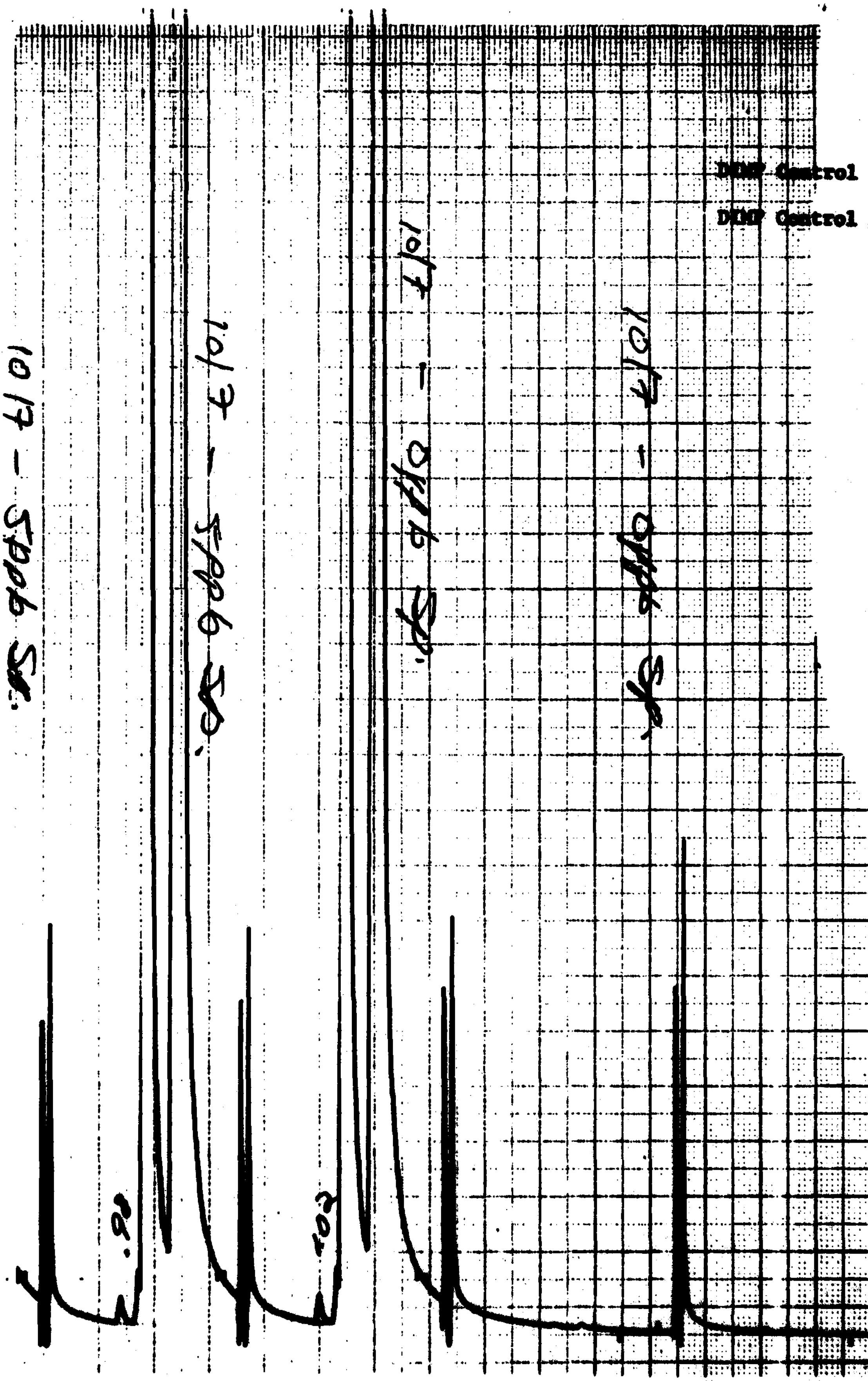
Example Chromatograms of 50 ppb 100 ppb mixtures of DIMP, DMMP and TMP

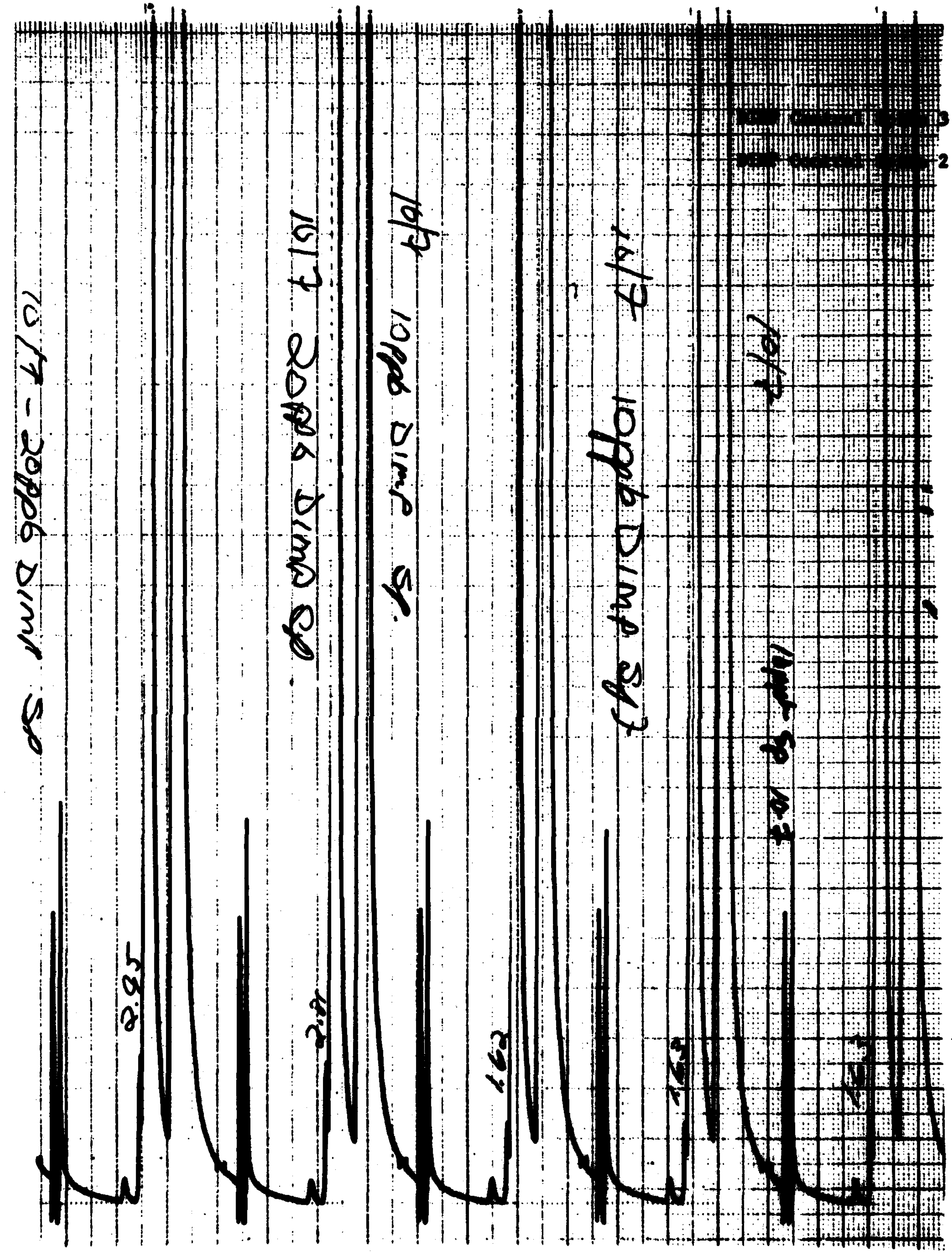


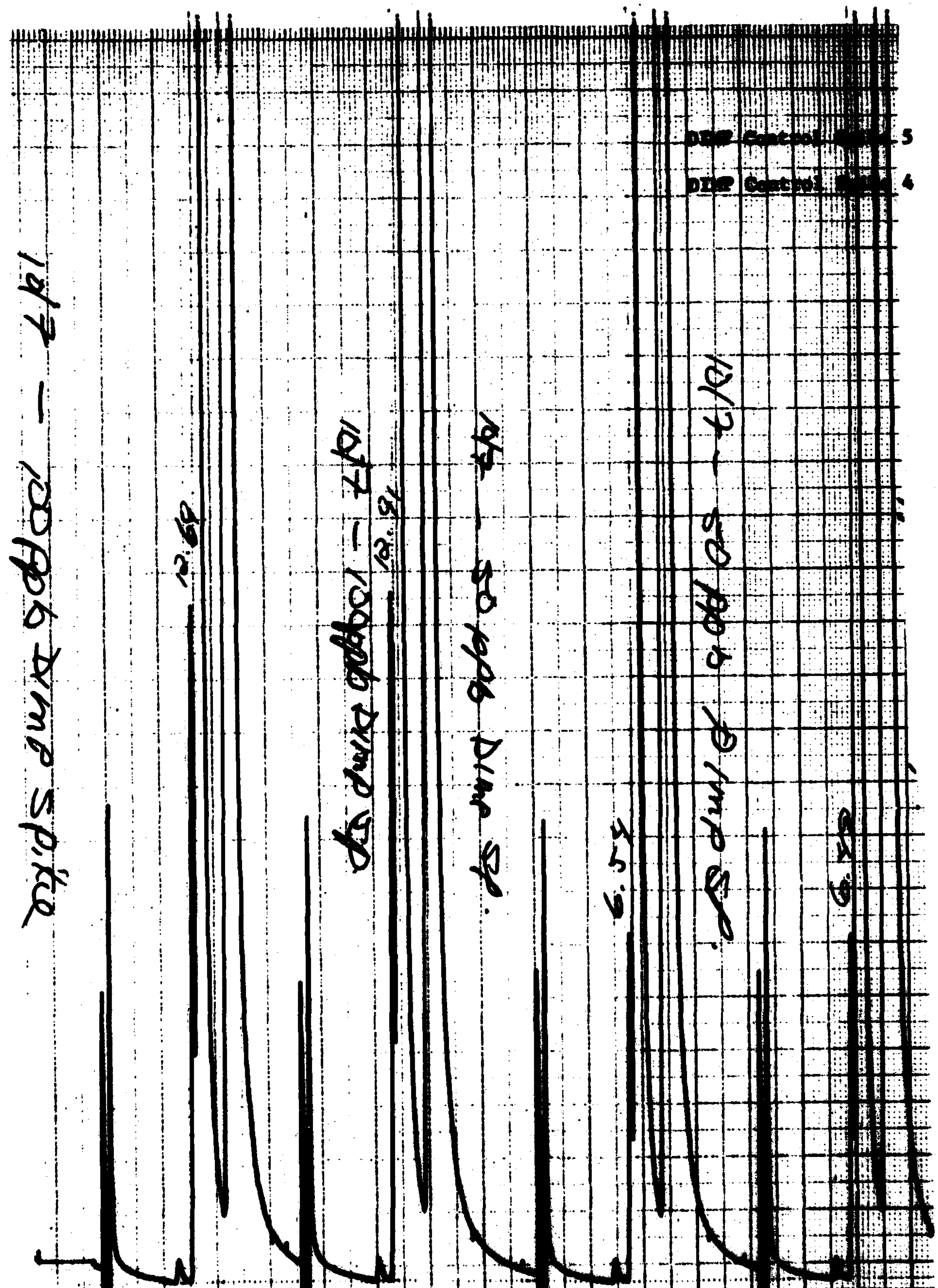
DIMP CAL STD 2




DIMP CAL STD 4
Acetone Blank
CH_2Cl_2 Blank


DIMP Control Spike 1
DIMP Control Blank


10/7 - 20ppb DIMP Sp
2.85
10/7 20ppb DIMP Sp
2.87
10/7 10ppb DIMP Sp.
1.63
10/7 10ppb DIMP Sp7
1.63
10/7
10ppb Sp 10-7


DIMP Control
5
DIMP Control
4

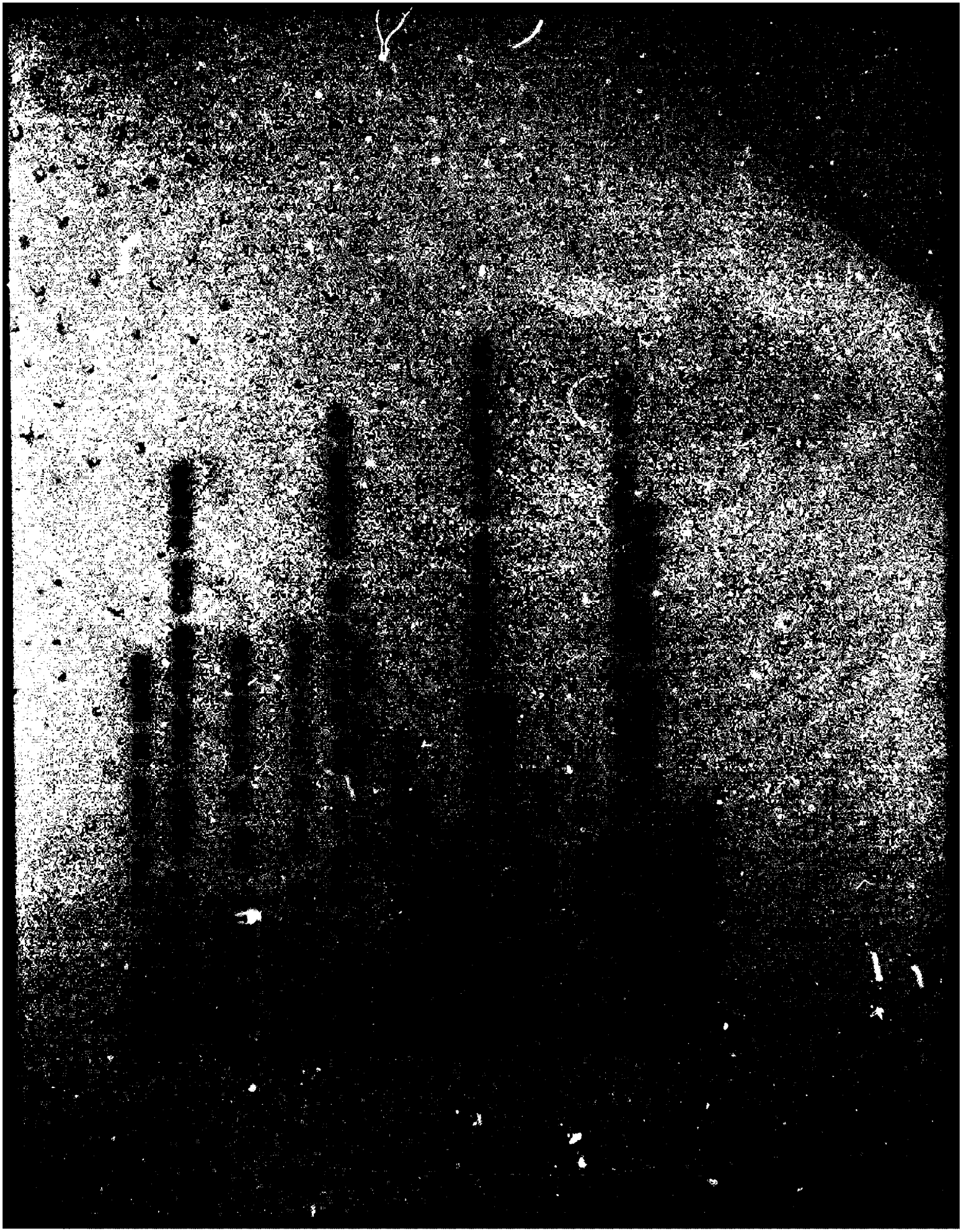
APPENDIX B

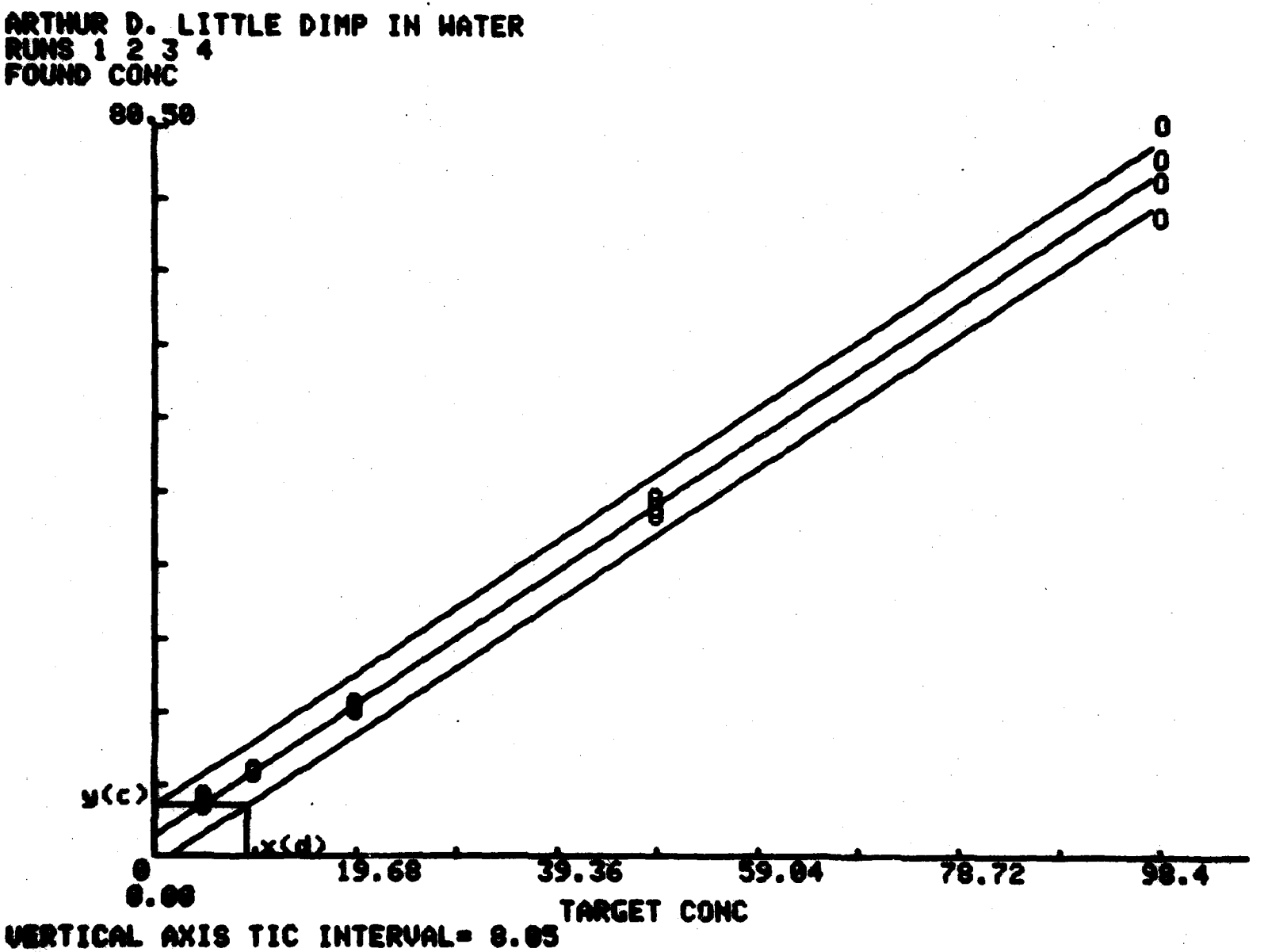
Precision and Accuracy Data Set

of Diisopropyl methylphosphonate

ARTHUR D. LITTLE DIMP IN WATER
RUNS 1 2 3 4
COMPILATION OF TARGET CONC. VS FOUND CONC

Target Conc UG/L	Day 1 Found Conc UG/L	Day 2 Found Conc UG/L	Day 3 Found Conc UG/L	Day 4 Found Conc UG/L
4.920	6.000	6.700	5.690	5.730
9.840	9.660	9.660	9.340	9.710
19.700	16.400	16.600	17.000	16.600
49.200	39.400	39.300	37.600	38.300
98.400	76.600	70.000	74.100	80.500

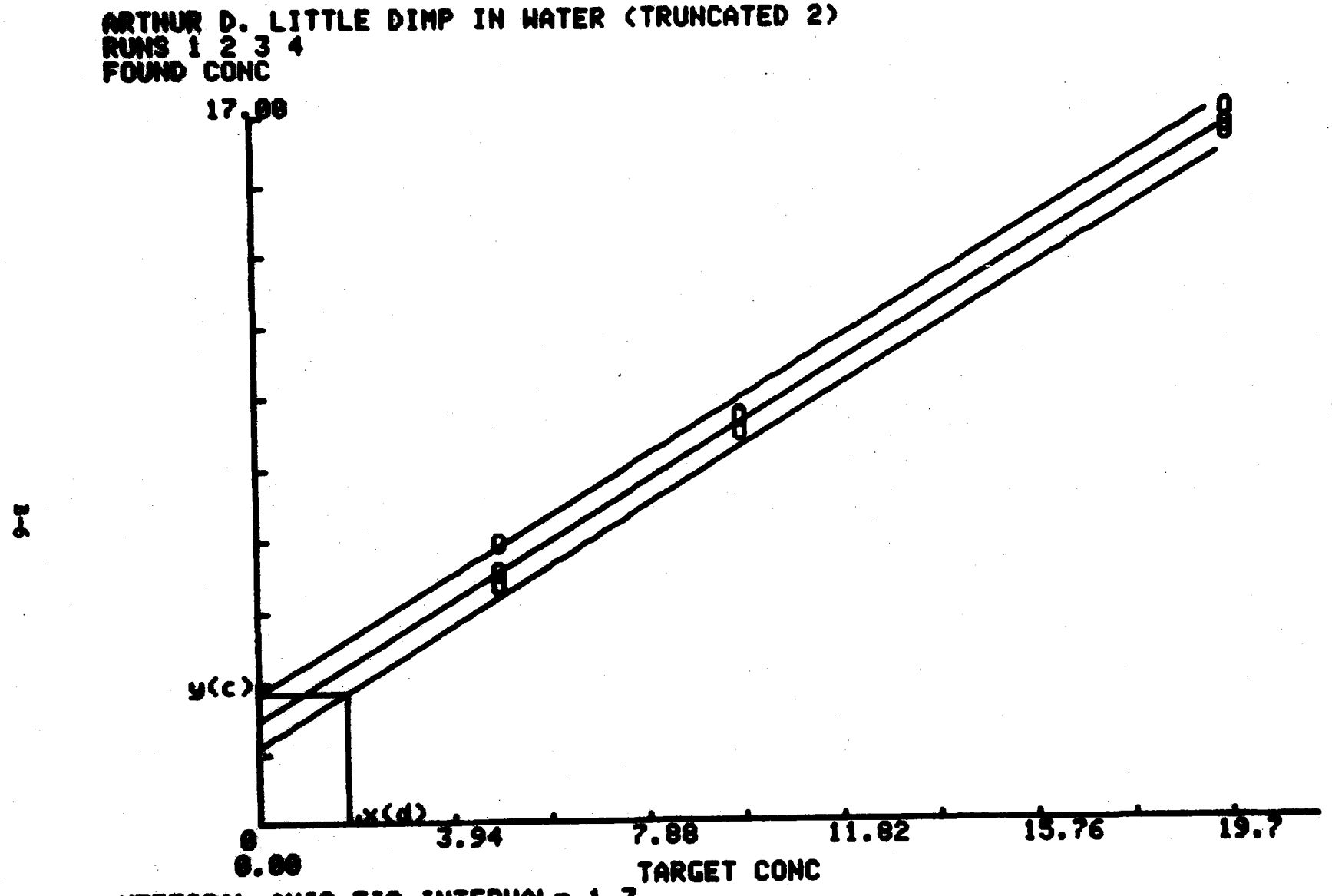



ARTHUR D. LITTLE DIMP IN WATER
RUNS 1 2 3 4
FOUND CONC
80.50
0
0
0
0
y(c)
x(d)
0
0.00
19.68
39.36
59.04
78.72
98.4
TARGET CONC
VERTICAL AXIS TIC INTERVAL= 8.05

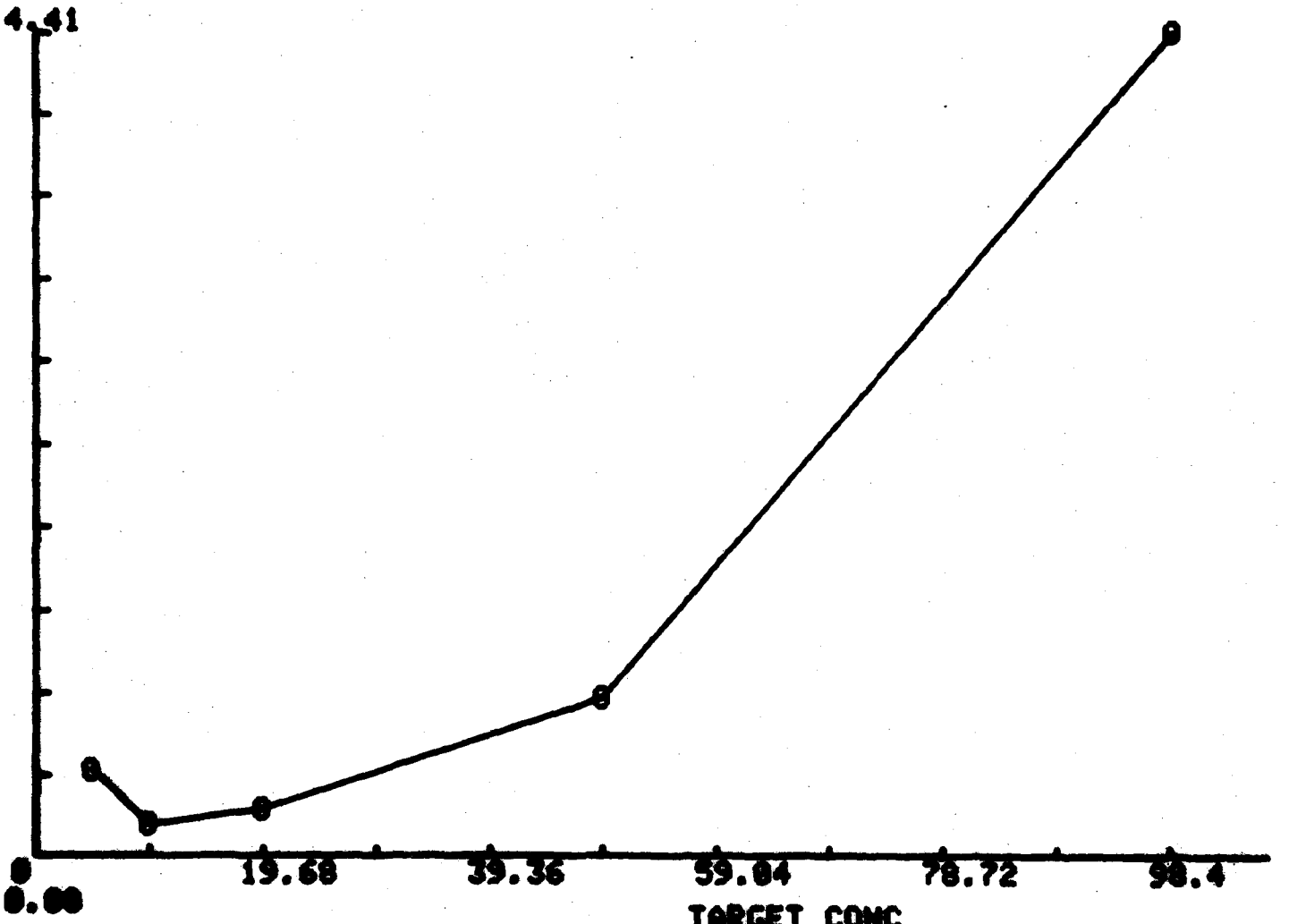
ARTHUR D. LITTLE DIMP IN WATER
RUNS 1 2 3 4
STATISTICAL DATA USED TO DETERMINE PERCENT INACCURACY AND IMPRECISION

Mn Targt Con UG/L	Mn Found Conc UG/L	Standard Deviation	Mean Pct Inaccuracy	Imprecision
4.920	6.030	0.467	22.561	7.751
9.840	9.592	0.170	-2.515	1.772
19.700	16.650	0.252	-15.482	1.511
49.200	38.650	0.858	-21.443	2.221
98.400	75.300	4.407	-23.476	5.852
Means		1.231	-8.071	3.822

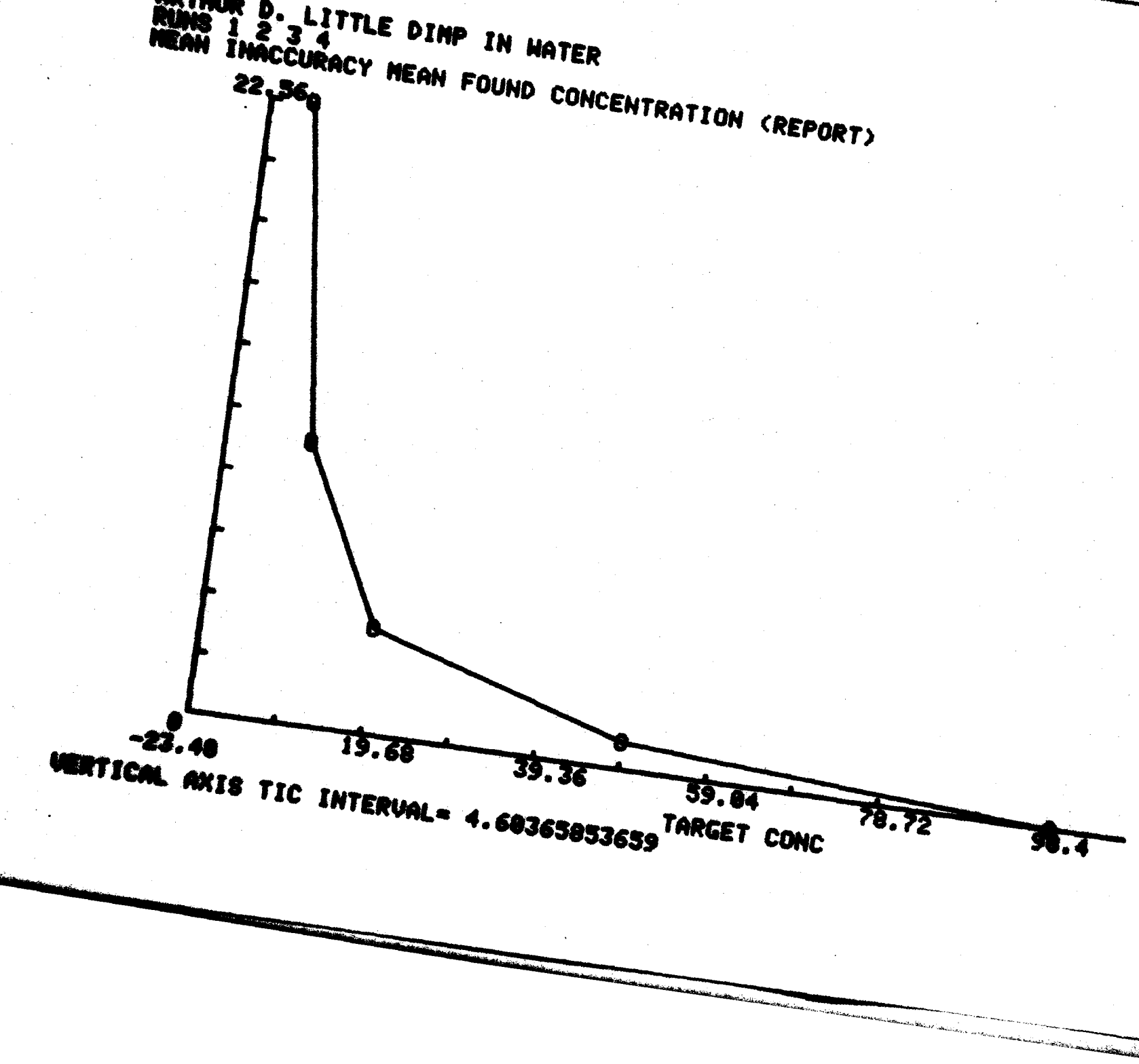
```
ARTHUR D. LITTLE DIMP IN WATER (TRUNCATED 2)
RUNS 1 2 3 4
ANALYSIS OF 12 TARGET CONC-FOUND CONC POINTS

TARGET CONC
MEAN= 11.4866666667  SD= 6.41848089268

FOUND CONC
MEAN= 10.7575  SD= 4.61858129536

NO. RUNS 4 TOTAL X-Y ALL RUNS 12 NO. CONCENTR 12
MEASURES (Y'S) EACH TARGET CONC 1

INTERCEPT= 2.5084432867
SLOPE= 0.71814190717
 USE FOR ACCURACY
R= 0.998007790302
MEAN SQR DEV OF POINTS FROM REGRESSION= 0.093398972168
ST ERROR EST= 0.30561245421
 USE FOR PRECISION
T FOR CONFIDENCE BAND
D.F.= 10
TWO TAIL P LEVEL IS .1
t= 1.81245868646
X(D) FOR CALIBRATION CURVE OR UNKNOWN SAMPLE? C/U C
(EACH TARGET CONC CONSIDERED INDEP SAMPLE
MEASURED 1 TIME(S))
y(c)= 3.15784045679
x(d)= 1.78073240852
```


ARTHUR D. LITTLE DIMP IN WATER (TRUNCATED 2)
RUNS 1 2 3 4
FOUND CONC
17.00
y(c)
x(d)
0
0.00
3.94
7.88
11.82
15.76
19.7
TARGET CONC
VERTICAL AXIS TIC INTERVAL= 1.7

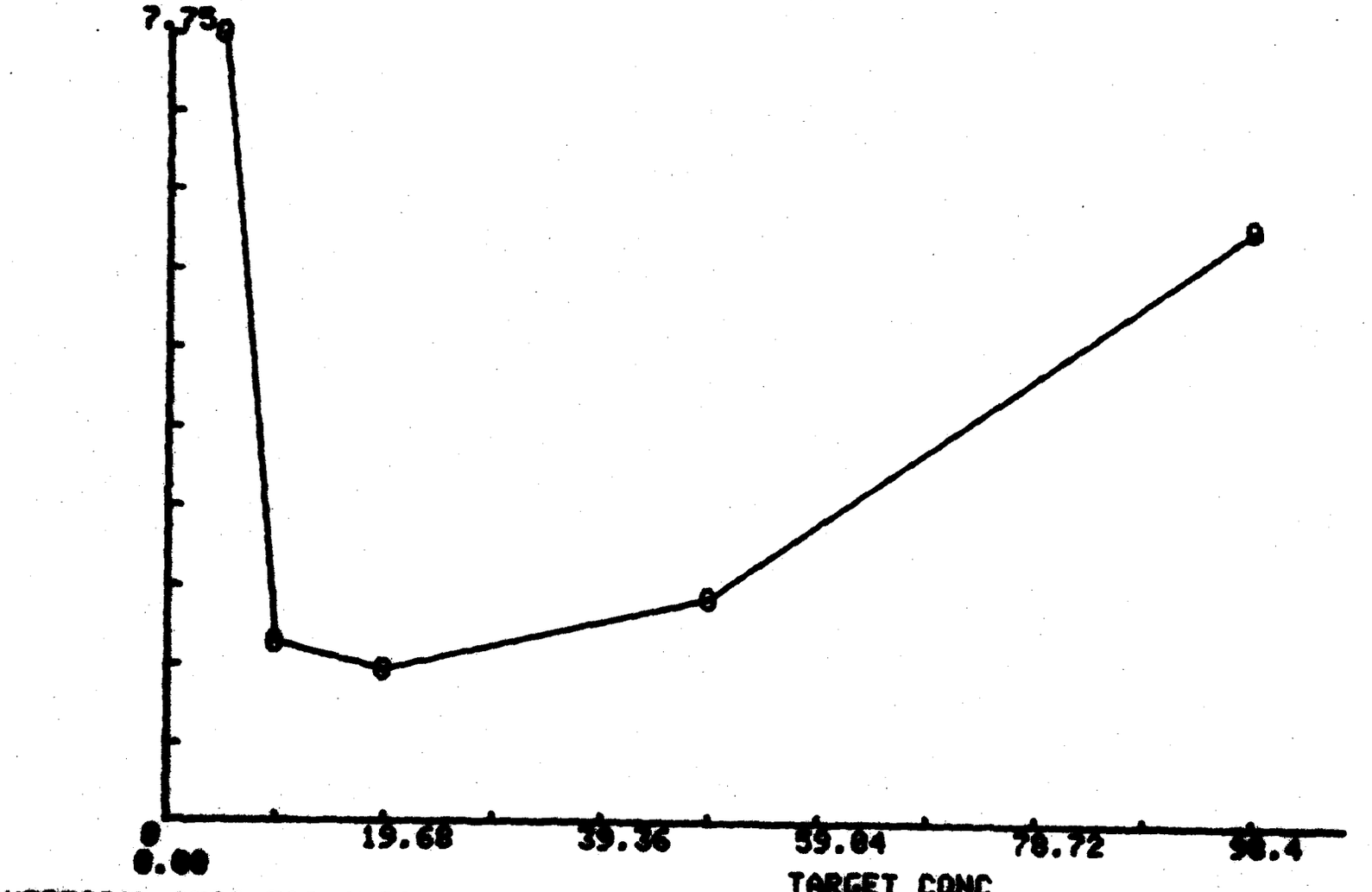
ARTHUR D. LITTLE DIMP IN WATER
RUNS 1 2 3 4
STANDARD DEVIATION MEAN FOUND CONCENTRATION (REPORT)



VERTICAL AXIS TIC INTERVAL= 0.440681290732


ARTHUR D. LITTLE DIMP IN WATER
RUNS 1 2 3 4
MEAN INACCURACY MEAN FOUND CONCENTRATION (REPORT)
22.56
-23.48
19.68
39.36
59.04
78.72
98.4
VERTICAL AXIS TIC INTERVAL= 4.60365853659
TARGET CONC

ARTHUR D. LITTLE DIMP IN WATER
RUNS 1 2 3 4
IMPRECISION MEAN FOUND CONCENTRATION (REPORT)



VERTICAL AXIS TIC INTERVAL= 0.77513130671

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